MEMBRANE SEPARATION PROCESSES FOR WASTEWATER TREATMENT

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At present, membrane processes, as well as research concerning various systems with synthetic and biological membranes, are very important and spread all around the world.

The membrane separations are used on large scale in water treatment for drinking and industrial purposes (desalination) and in wastewater purification. We can mention here membrane processes like electro dialysis with ionic exchange membranes (ED), reverse osmosis (RO), ultra filtration (UF), micro filtration (M) and dialysis with micro-porous membranes [1].

In the last years, research and development in this field not only did result in a better understanding of the involved fundamental knowledge, but also determined the set up of new treatment processes and configurations. The liquid surfactant (emulsion) membranes as a selective technique have a large potential for application in wastewater treatment.

Emulsion liquid membrane (ELM) technique is applied both for some waters with organic or inorganic pollutants and for some waters with pollutant mixtures. The method is especially applicable for heavy metal separation from aqueous solutions. In addition, the separated water can be recycled in the process. The membrane method has been applied to some water containing ferrous and non-ferrous metals, alkaline metals, radioactive elements, rare metals, etc.

Liquid membranes offer large possibilities for selective separation and concentration of pollutants from dilute aqueous solutions (wastes) resulting in high treatment efficiencies. By LM process, it is possible to realise simultaneously wastewater purification and recovery of some separated impurities in form of utilisable concentrated solutions.

The principle of ELM unit process is pollutant mass transfer from water to be treated (external phase, feed phase) in an internal aqueous phase (stripping phase, receiving phase), suited for an irreversible capture of transported species.

Thus, the process reagents (surfactant, carrier and receiving agent within the internal phase) impose the mass transfer direction. The surfactant stabilises the liquid membrane and the carrier enhances the transfer of some species through organic phase (liquid membrane).

The amount of pollutant transferred into the receiving phase depends on the hydrodynamic conditions. The pollutant mass transfer between the two aqueous phases occurs by a selective permeable barrier, i.e. an organic phase (liquid membrane). The organic phase is prepared previously in the form of continuous thin films. They are placed in such a way that one interface is next to continuous layers of the feed phase, and the opposite one is near the internal phase in form of individual micro drops (droplets).

The method for generating the double emulsion system follows after the step of primary emulsion formation (liquid membrane) by external energy contribution and the step of its distribution into the water to be treated [2-3].

Our team has studied the separation of various chemical species in water by membranes process for a long time. At first, we dealt with the separation and recovery of metallic ions (Ni^{2+}, Zn^{2+}) from industrial wastewaters using electrodialysis with ion exchange membranes. The results were very promising.

We have used liquid membrane separation of different pollutants from wastewaters since 1988 (e.g., cations and/or anions (Co^{2+}, Cu^{2+}, Ni^{2+}, Ag^{+}, Cr^{6+}, and Pb^{2+}), organic substances (amines, acetic acid), or inorganic and organic mixtures. We tried to identify and estimate a series of factors that influenced the mass-transfer from the giving (feed) phase of chemical species (wastewater) to receiving and concentrating phase (emulsion liquid phase). The triad: adequate reagents-time-hydrodynamic regime was considered an important link in the chain of the mass-transfer of a species in the desirable direction.

The treatment method of wastewaters by liquid membrane was very simple, rapid and efficient. Difficulties in the application of this method did not consist in sophisticated equipment or installations. They consisted in the adequate choice of reagents to allow the selective extraction of pollutants in requested quantity and time. To these considerations, some hydrodynamic conditions were added, which influenced on the reagent and time choice.

The above-mentioned triad was specific for each water sample and each pollutant to be removed (concentrated and/or recovered from water). There were a multitude of working possibilities to satisfy the requirements of efficiency, simplicity and rapidity.

Our experiments with synthetic water containing Cu^{2+} ions (0.6-0.8 mg/L) allowed finding some working conditions for ELM separation, which proved the above-mentioned requirements of the method. In this case the studies showed that by choosing adequate and efficient reagents, time interval and energy range of ELM method were larger and therefore it was not necessary a rigorous control.

In addition, the use of some reagents having a large spectrum of application required either a specific time or a specific hydrodynamic regime, and even both of them.

The double emulsions type water/oil/water were organised as thin films and the mass transfer process was influenced by permeation phenomena and by the value of the repartition coefficient of the involved species.

For example, to separate and concentrate Cr (VI) species within the internal phase, the transport through interfaces and in the bulk was studied by working with some appropriate extraction and transport agents (ammonium quaternary salts of type $R_3NH^+X^-$, where X was Cl^- or HSO_4^-)[4-7].

An important role for the mass transfer of Cr (VI) species was played by the characteristics of surfactants used for obtaining of the primary emulsion water/oil. The surfactants used were various types of Span 80 (sorbitol mono-, di- and tri-oleate) having HLB between 4.3-5.6.

The use of ammonium quaternary salts and Spans 80 showed synergy phenomena of mass transfer of Cr (VI) species.

The experimental method established the concentration ranges for the surfactant. The concentration ranges for ammonium quaternary salt were as follows:

- Carrier concentration lower than 0.005% wt. versus to the primary emulsion, where the efficiency ranged 25- 50 %
- Carrier concentration ranged 0.005-0.01% wt. versus to the primary emulsion, where the efficiency ranged 50-90 %;
- Carrier concentration ranged 0.01-0.05% wt. versus to the primary emulsion, where the efficiency ranged 85-99 % .
- Carrier concentration ranged 0.05-1% wt. versus to the primary emulsion, where the efficiency ranged 85-99 %

For carrier concentrations lower 0.05% wt. versus to the primary emulsion, molar ratio (Cr(VI)/TOA) ranged 100-800. The transport mechanism by micelle was supposed .

The efficiencies over 50% it was obtained for carrier concentrations higher 0.005 %.

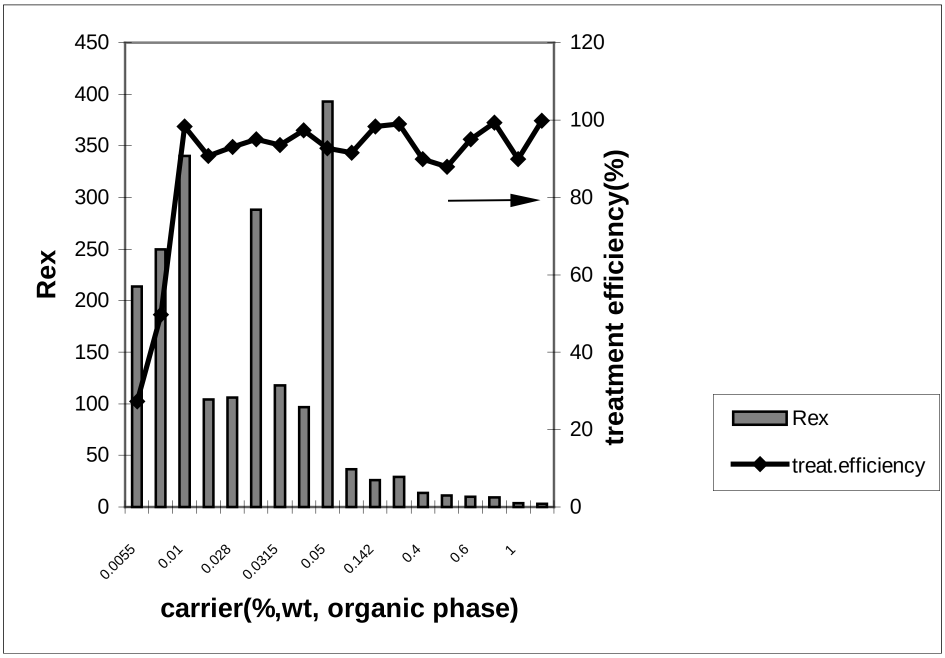

Figure 1. Illustration of the concentrations ranges of TOA for Cr(VI) mass transport at 25 °C

The date in Figure 1 allowed the assessment of the carrier amount on the treatment efficiency for ELM technique. Three concentration ranges could be noticed. The first concentration range was 0.005-0.01% wt. with respect to the organic phase and the molar ratio Cr(VI):TOA ranged between 350-500. The second concentration range was 0.01-0.05% wt. with respect to the organic phase and molar ratio Cr(VI):TOA ranged between 100-250. The third concentration range was 0.05-1% wt. with respect to the organic phase and molar ratio Cr(VI):TOA ranged between 1-2.0.

Both the treatment efficiency reached 90-99% and molar ratio(Cr(VI)/TOA) ranged 100-500 correspond to the critical micelle concentration range of the carrier.

Duration over 10 minutes led to side processes as water transfer mediated by surfactant and carrier. The ELM technique used for synthetic water allowed additionally the treatment of some industrial wastewaters (6-92 mM). The variation of the working conditions allowed treatment efficiencies ranging between 89-99%. The concentrating factor was 1.5-3.65

CONCLUSION

The permeation processes carried out by the ELM technique correlated with the working ratio, the pollutant amount within the feed phase and the duration. The mass transfer of Cr(VI) by the ELM technique was accomplished by carrier agents.

For carrier concentrations lower 0.05% wt. versus to the primary emulsion, molar ratio (Cr(VI)/TOA) ranged 100-800. The transport mechanism by micelle was supposed .

The first concentration range lower than 0.005% wt. with respect to the organic phase and the molar ratio ranged between 500-800. The second concentration range was 0.005-0.01% wt. with respect to the organic phase and the molar ratio Cr(VI):TOA ranged between 350-500. The third concentration range was 0.01-0.05% wt. with respect to the organic phase and molar ratio Cr(VI):TOA ranged between 100-250. The fourth concentration range was 0.05-1% wt. with respect to the organic phase and molar ratio Cr(VI):TOA ranged between 1-2.0.

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